



Electrospun polyacrylonitrile nanofibers supported Ag/Pd nanoparticles for hydrogen generation from the hydrolysis of ammonia borane

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HIGHLIGHTS

- The electrospun nanofibers were firstly used for the hydrogen generation.
- Ag/Pd NPs were uniformly distributed on the surface of the PAN nanofibers.
- The PAN/Ag/Pd composite nanofibers exhibited excellent catalytic activity.
- Good recycle stability and easy separation from the reacted system was achieved.

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ABSTRACT

A high-performance hydrogen generation system based on the electrospun polyacrylonitrile (PAN)/Ag/Pd composite nanofibers, which were prepared by microwave reducing the electrospun PAN/AgNO₃ nanofibers and followed by a replacement reaction has been demonstrated. The morphology of the as-prepared PAN/Ag/Pd composite nanofibers and the metal nanoparticles on the fibers were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), high resolution TEM (HRTEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) measurements. It has been demonstrated that the obtained PAN/Ag/Pd composite nanofibers possess fine morphology and high catalytic activities for H₂ generation from aqueous solution of ammonia borane (NH₃BH₃, AB). The H₂ generation test exhibited that the catalyst had excellent catalytic activity (with turnover frequency (TOF) of 377.2 mol H₂ h⁻¹ (mol Pd)⁻¹), good recycle stability and easy-separation from the reaction system. This new kind of nanofibers possesses great potential application for the new clean energy development.

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1. Introduction

Today's world is experiencing acute energy shortage. So developing new, clean and environmentally friendly energy is extremely urgent. As one of the most important alternative energy carriers, hydrogen is considered to be one of the best candidates to satisfy the demand for future energy crisis [1]. However, the wide usage of hydrogen is restricted by the deficiencies of reliable H₂ generation and storage methods. Recently, ammonia borane (NH₃BH₃, AB) has attracted extensive attention due to its high hydrogen content (19.6 wt%) which exceeds the gasoline and makes itself a promising candidate for chemical hydrogen-storage applications. Meanwhile,

its nontoxicity, good stability at room temperature, easy storage and the kinetic properties under moderate conditions are also attractive [2–6]. Considering AB is relatively stable in aqueous solution under the normal condition, catalysts are necessary to be required to accelerate the rate of hydrogen release reaction.

Despite all the advancements in catalyst preparation, there is still great interest in developing catalytic supporters from stable and inert nanofibers because such nanofibers can provide more positions and large surface area for catalytic reaction. In the past few years, electrospinning technique has been proven to be a simple and feasible method for synthesizing continuous polymeric nanofibers with a high specific surface area to volume ratio and high porosity [7]. Polymeric nanofibers have various kinds of applications including textile devices [8,9], sensors [10], biomedical applications [9,11] and filtration [10–13]. Furthermore, the nanofibers have also been shown to be very useful for heterogeneous

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catalysis [14]. The nonwoven materials have been proven to be efficient catalysts supporters for catalytic metal nanoparticles and easy to recycle for reusing [15]. However, few works about the application of the electrospun nanofibers as catalytic supporters for noble metal nanoparticles to generate hydrogen from the hydrolysis of ammonia borane have been reported.

In this paper, we have successfully fabricated PAN/Ag/Pd composite nanofibers by an electrospinning process and put them for the catalysis of hydrogen generation for the first time. Firstly, we prepared PAN/Ag nanofibers by microwave heating the electrospun PAN/AgNO₃ nanofibers. Then, the PAN/Ag/Pd nanofibers were achieved by a galvanic replacement reaction between Ag nanoparticles on the surface of PAN nanofibers and Na₂PdCl₄. The as-prepared PAN/Ag/Pd composite nanofibers exhibited an excellent catalytic performance toward H₂ generation from aqueous solution of AB which proposed a new method in this field.

2. Experimental section

2.1. Chemicals

Polyacrylonitrile ($M_w = 80,000$) fibril constitutive of acrylonitrile (91%), acrylamide (8.5%), and itaconic acid (0.5%) was

purchased from Jilin Chemical Plant. N,N-Dimethylformamide (DMF) was obtained from Tianjin Tiantai Refine Chemicals Co., Ltd. AgNO₃ was purchased from Shanghai Chemical Reagent Co., Ltd. Ethylene glycol and sodium hydroxide were both acquired from Beijing Chemical Works. Sodium tetrachloropalladate (II) (Na₂PdCl₄) was purchased from Aladdin. Ammonia-borane (NH₃BH₃, 90%) was obtained from Aldrich. Distilled water was used throughout the experiments.

2.2. Preparation of PAN/Ag composite nanofibers

In a typical experiment, PAN/Ag composite nanofibers were prepared from PAN/AgNO₃ nanofibers which were fabricated via electrospinning process. During this process, 0.7 g of PAN and 12 mL of DMF were mixed in a conical flask followed by stirring for 4 h at 60 °C in order to form homogeneous solution. Then 0.3 g of AgNO₃ was put into the above colloidal solution when it cooled down to the room temperature. After stirring for 8 h in the darkness, a light yellow solution was obtained.

Then the solution was transferred into a glass needle. An appropriate voltage of 15 kV was employed between the needle and the collected aluminum foil with a distance of 20 cm so that the PAN/AgNO₃ nanofibers could be achieved on the collected foil. The obtained nanofibers were used as raw materials.

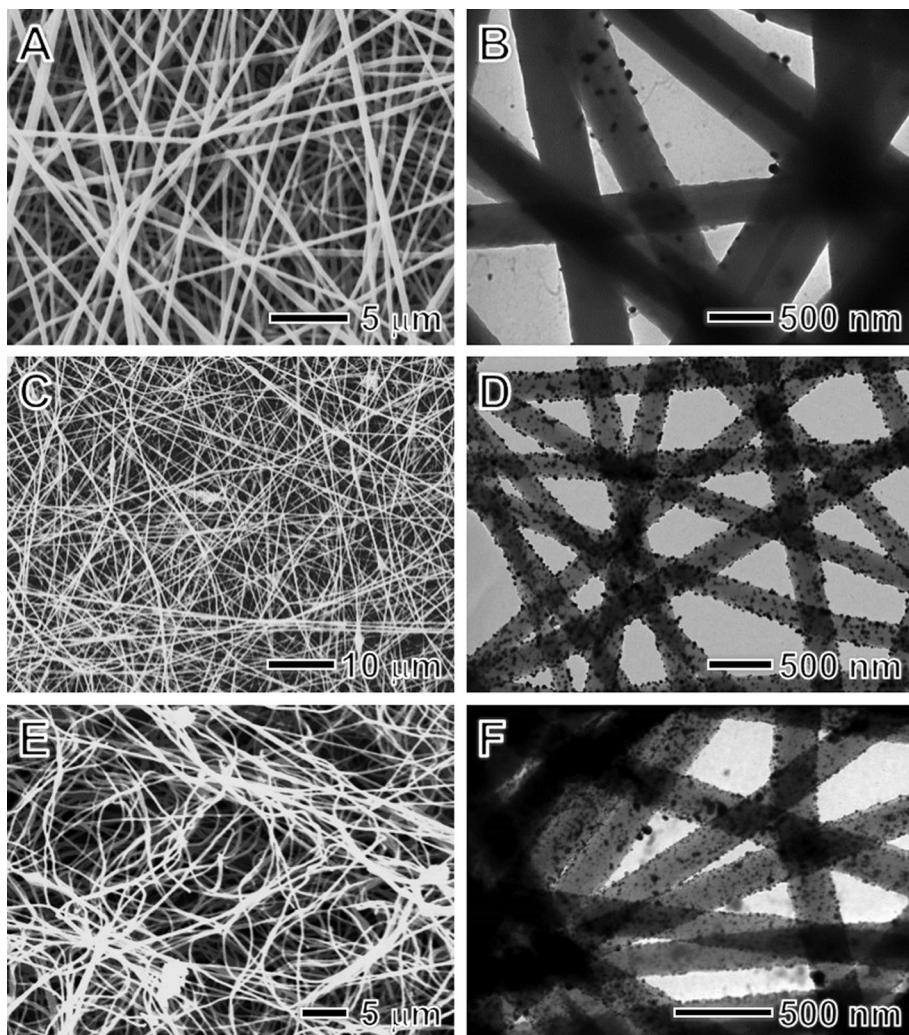


Fig. 1. SEM and TEM images of PAN/AgNO₃ nanofibers (A and B), PAN/Ag nanofibers (C and D), PAN/Ag/Pd nanofibers (E and F), respectively.

In another flask, 0.16 g of NaOH and 20 mL of ethylene glycol were mixed and transparent solution could be formed after 2.0 h of stirring at room temperature. Then the prepared PAN/AgNO₃ nanofibers were put into this homogeneous solution and the container was heated in the center of a microwave oven for 20 s. During the heating process, color of the nanofibers gradually turned to brown because the AgNO₃ was reduced to Ag nanoparticles. Then the achieved PAN/Ag nanofibers needed to be washed by distilled water for several times in order to remove the remaining impurities and then dried in air for further using.

2.3. Preparation of PAN/Ag/Pd composite nanofibers

To prepare PAN/Ag/Pd composite nanofibers, 25 mL of water containing excessive Na₂PdCl₄ was initially injected into a three-necked flask (fitted with a reflux condenser and a proper size magnetic stirrer) along with 5 mg of the fibers and heated in an oil bath at 120 °C for 1 h. After cooling down to the room temperature, the fibers should be soaked in saturated salt water and distilled water for 24 h, respectively, to remove the formed AgCl and other residues. Moreover, the nanofibers should also be washed by distilled water for several times and dried in air for the further test.

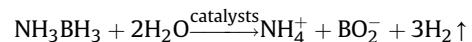
2.4. Characterization of PAN/Ag/Pd composite nanofibers

The transmission electron microscope (TEM) images of PAN/Ag/Pd nanofibers were determined by JEM-1200EX (JEOL, Japan) with an acceleration voltage of 100 kV. The surface morphological characterization of nanofibers was examined by means of scanning electron microscopy (SEM, SSX-550, Shimadzu, Japan). HRTEM

imaging and energy dispersive X-ray (EDX) analysis were performed on a FEI Tecnai G2 F20 high-resolution transmission electron microscope operating at 200 kV. X-ray data were collected by using an X-ray diffractometer (Empyrean, PANalytical B.V.) based on Cu-K α radiation. The 2 θ angle of the diffractometer was stepped from 10° to 90°. XPS data of the materials was obtained by Thermo Scientific ESCALAB250 measurement. The weight percentages of Ag and Pd in the nanofibers were determined by inductively coupled plasma (ICP) atomic emission spectrometric analysis (PerkinElmer OPTIMA 3300DV).

2.5. Hydrogen generation

The hydrolysis reactions of aqueous NH₃BH₃ with as-prepared PAN/Ag/Pd nanofiber catalysts were carried out at room temperature and normal atmospheric pressure. During this process, 6.2 mg of PAN/Ag/Pd nanofibers were placed in a flask which contained 0.096 g of NH₃BH₃ with weight ratio of 0.022 (metal/AB) and AB was dissolved in water with a weight ratio of 1%. Drainage was used to measure the volume of H₂. The reaction between NH₃BH₃ and water was as follows [16]:



2.6. Recycle stability

When the first hydrogen generation reaction was completed, the as-prepared PAN/Ag/Pd nanofibers could be grabbed with tweezers. Then the nanofibers needed to be washed with distilled water for several times for reusing. And then a new AB aqueous

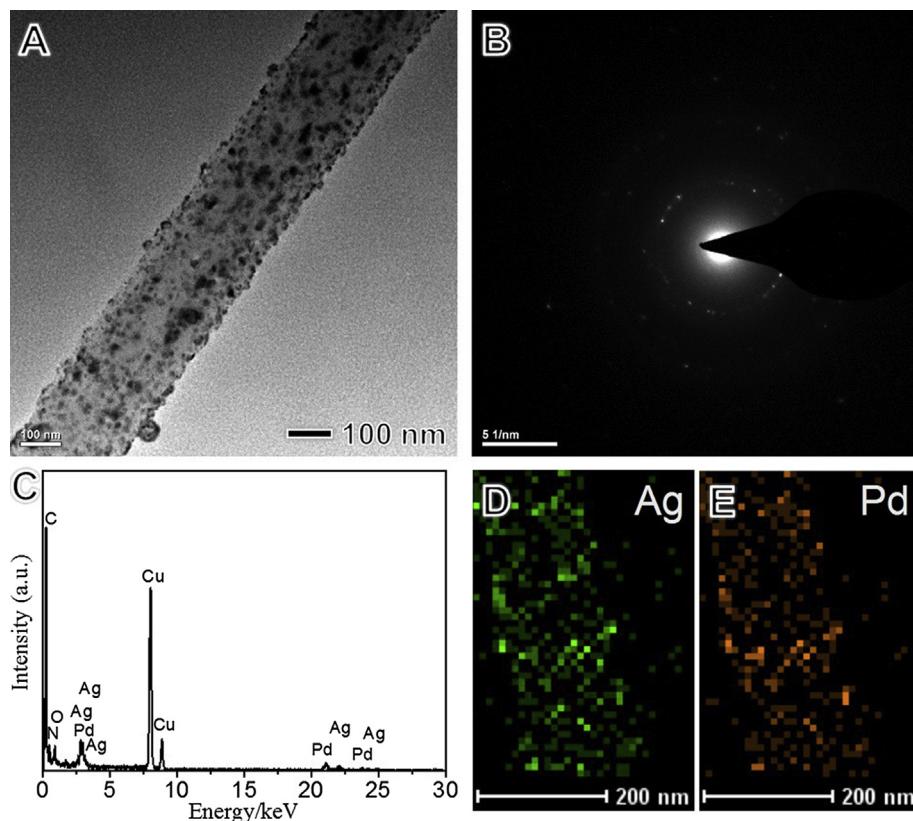


Fig. 2. (A) HRTEM image of the PAN/Ag/Pd nanofibers; (B) the FFT of the nanofibers; (C) EDX spectra of the PAN/Ag/Pd nanofibers; ((D) and (E)) EDX mapping images of the PAN/Ag/Pd composite nanofibers.

solution as before and the same nanofibers were added into the flask to regenerate hydrogen again instantly. The evolution of gas was monitored by drainage method. Such recycle experiments were repeated for five times under ambient atmosphere at room temperature.

3. Results and discussion

3.1. Preparation and characterization of the electrospun PAN/Ag/Pd composite nanofibers

The PAN/Ag composite nanofibers were prepared by electrospinning a mixed solution containing PAN, AgNO₃ and DMF, then followed by a microwave reduction process. Fig. 1A and C showed the SEM images of the electrospun PAN/AgNO₃ composite nanofibers before and after the microwave irradiation treatment. It was found that the surface of the PAN/AgNO₃ nanofibers was smooth and their diameters were uniform within a range of 200–500 nm, which was also proved by a TEM image simultaneously (Fig. 1B). The TEM image also showed that a small amount of metal nanoparticles appearing on the surface of PAN/AgNO₃ nanofibers, which could be attributed to the reduction of AgNO₃ by the light during the electrospinning and operation process. After the microwave reduction, the morphology of the nanofibers almost did not change, but the diameters of nanofibers were shrunk to 200–400 nm and a large quantity of Ag nanoparticles were generated and distributed uniformly on the surface of PAN nanofibers which was exhibited in Fig. 1D. The diameters of the obtained Ag nanoparticles were in the range of 5–10 nm. The PAN/Ag/Pd composite nanofibers could be prepared by a galvanic replacement reaction between the PAN/Ag composite nanofibers and Na₂PdCl₄. Fig. 1E and F presented the typical SEM and TEM images of the as-prepared PAN/Ag/Pd composite nanofibers. It was found that the net structure of the nanofibers was kept and the obtained Ag/Pd nanoparticles were distributed uniformly on the surface of PAN nanofibers. The HRTEM image was further used to study the PAN/Ag/Pd nanofibers. The diameters of the Ag/Pd nanoparticles were estimated in the range of 5–20 nm and some of the particles were slightly agglomerated (Fig. 2A). The FFT (Fast Fourier Transform) of the Ag/Pd nanoparticles further proved their good crystallinity (Fig. 2B). Furthermore, the energy-dispersive X-ray spectroscopy (EDX) also confirmed the fact that the element of Ag and Pd existed in and on the PAN/Ag/Pd composite nanofibers (Fig. 2C). The signal of Cu in the EDX spectrum originated from the carbon-coated copper grid. This result confirmed that the Pd nanoparticles had been successfully prepared in the PAN/Ag/Pd composite nanofibers. The EDX mapping analysis revealed that the Ag and Pd components were

homogeneously distributed throughout the PAN/Ag/Pd composite nanofibers, respectively. The weight percentages of Ag and Pd in the PAN/Ag/Pd composite nanofibers were also determined by ICP measurement, which gave values of about 6.5% and 27.1%, respectively.

Fig. 3 showed the XRD patterns of the as-spun PAN/AgNO₃, PAN/Ag and PAN/Ag/Pd nanofibers obtained by the electrospinning technique, subsequent microwave reduction and replacement reactions. The spectrum of PAN/AgNO₃ was the same as usual polymer which showed only diffuse X-ray peak without any crystallization peaks. After heating in the microwave oven, the resulting diffraction peaks of PAN/Ag nanofibers at about $2\theta = 38.4^\circ, 44.4^\circ, 64.8^\circ, 77.7^\circ, 81.9^\circ$ were observed, which could be indexed to Ag (111), Ag (200), Ag (220), Ag (311) and Ag (222), respectively. In contrast, the diffraction peaks of PAN/Ag/Pd nanofibers showed the Pd (111) assigned at about $2\theta = 39.7^\circ$ except the peaks of Ag, which confirmed that the Pd nanoparticles were obtained successfully on the surface of the PAN nanofibers.

The X-ray photoelectron spectroscopy (XPS) was further used to characterize the chemical state of Ag and Pd nanoparticles and other ingredients in the PAN/Ag/Pd composite nanofibers. It was found that the peaks of Ag, Pd, Cl, N, O and C elements were obviously observed in the XPS spectra (Fig. 4A). Fig. 4B showed high

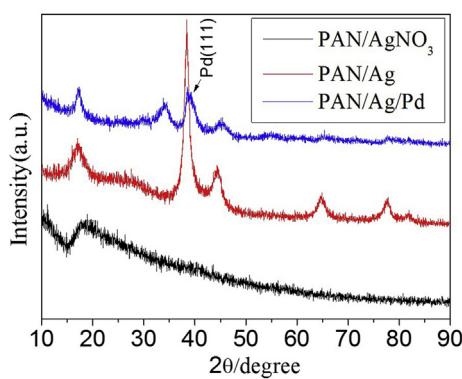


Fig. 3. XRD patterns of the prepared electrospun PAN/AgNO₃, PAN/Ag and PAN/Ag/Pd composite nanofibers.

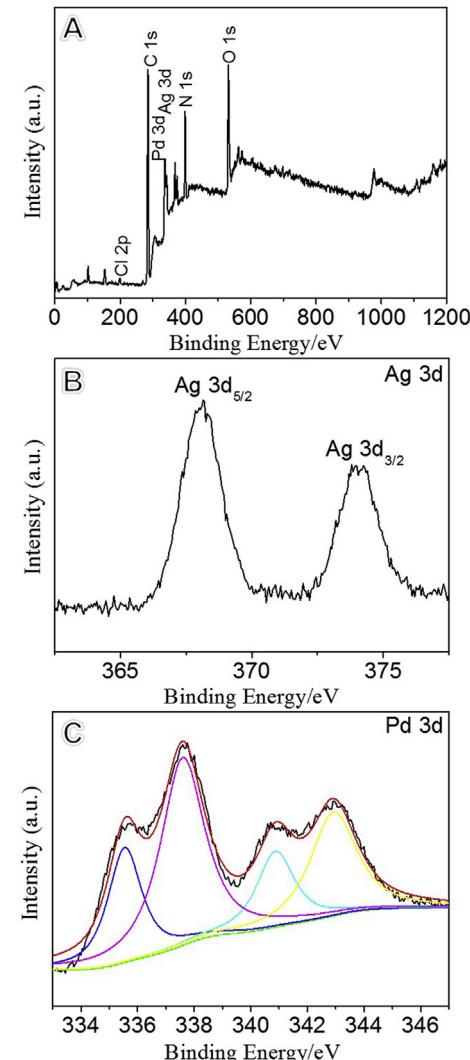


Fig. 4. XPS spectra of the obtained (A) PAN/Ag/Pd nanofibers; (B) Ag 3d; (C) Pd 3d.

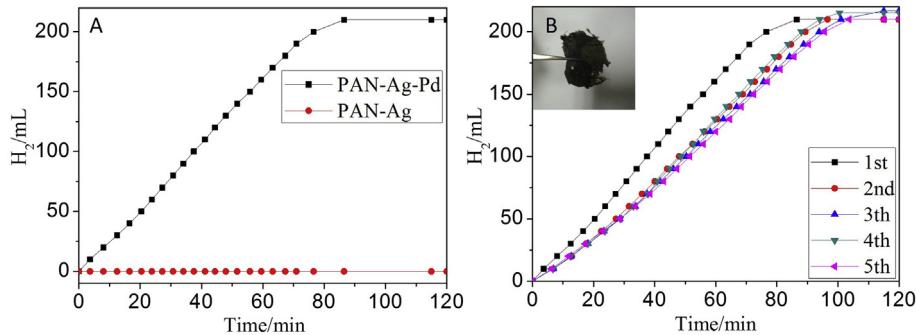


Fig. 5. (A) Hydrogen generation profiles with time in the presence of PAN/Ag/Pd nanofibers and PAN/Ag nanofibers; (B) 5 times of recycling test. Insert, the PAN/Ag/Pd nanofibers after 5 times of test.

resolution XPS spectrum of Ag element that the binding energies were 368.2 eV and 374.0 eV for Ag 3d_{5/2} and Ag 3d_{3/2}, respectively [17]. Fig. 4C exhibited the XPS patterns of Pd 3d with binding energy at 337.7 eV and 343.0 eV for palladium (II), and the bands at 335.7 eV and 340.9 eV are attributed to Pd (0), which further confirmed that Pd nanoparticles were present [18]. It should be noted from the XPS spectrum of Cl 2p illustrated in Fig. 4A that Cl element was the residual or the ingredient AgCl of reduction reaction and the intensity of Cl element was small, indicating the little content of Cl element in the PAN/Ag/Pd nanofibers. These results proved that the PAN/Ag/Pd composite nanofibers have been successfully prepared.

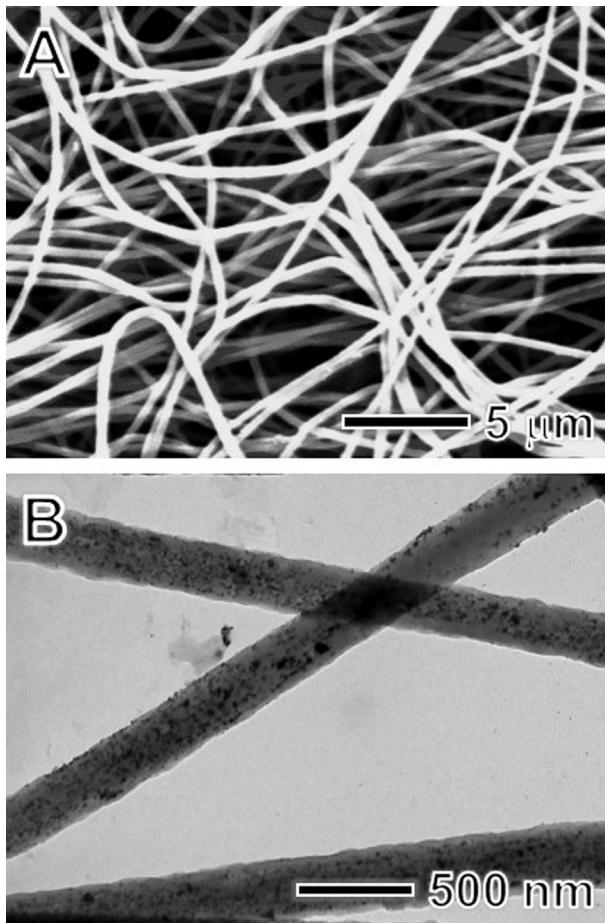


Fig. 6. ((A) and (B)) SEM and TEM images of PAN/Ag/Pd nanofibers after the fifth catalytic reaction.

3.2. Catalytic activities

The as-prepared PAN/Ag/Pd composite nanofibers have been used as catalysts for H₂ generation from the hydrolytic dehydrogenation of AB. We have compared the catalytic activities of PAN/Ag/Pd nanofibers with PAN/Ag nanofibers in the hydrogen generation process. Aqueous solution of AB released stoichiometric amount of hydrogen that mol H₂/mol AB was 3.0 according to the chemical equation. Fig. 5A exhibited the hydrogen generation profiles with time for the reactions of the hydrolytic dehydrogenation of AB (1.0 wt%) in the presence of PAN/Ag/Pd nanofiber catalysts and PAN/Ag nanofiber catalysts. It was noted that the PAN/Ag/Pd nanofibers showed a significant enhancement of activity in this test that finishing generating hydrogen reaction (about 210 mL H₂) in 86.5 min with turnover frequency (TOF) [19] of 377.2 mol H₂ h⁻¹ (mol Pd)⁻¹. However, the PAN/Ag nanofibers without Pd nanoparticles gave no hydrogen in 2 h and finally the system produced about 10 mL H₂ after 24 h. So it was taken consideration that the enhancement of catalytic activity of the PAN/Ag/Pd nanofibers was attributed to the loading of Pd nanoparticles. In addition, it is well known that the work function of Ag (111) was much lower than that of Pd (111), so charge transfer would occur from Ag to the Pd component, enhancing the adsorption of bridging AB molecules, which was also in favor of the good catalytic performance of the PAN/Ag/Pd nanofibers [20,21].

Furthermore, recyclability was also very important to every catalyst in practical application. The most significant advantage of the PAN/Ag/Pd composite nanofibers as catalyst for the hydrolytic dehydrogenation of AB was that it could almost keep the same high activity even after five times of recycling (Fig. 5B) and it also could be easily recycled by tweezers (Fig. 5B inset). From Fig. 5B, it was clearly seen that the reaction could be finished based on the as-prepared PAN/Ag/Pd composite nanofibers catalyst in 86.5 min for the first time. Then the next four times recycling reaction showed similar time but a little slower than the first time. However, the rate of hydrogen generating was still considerable. During the catalytic reaction, the morphology stability of the catalyst was of importance for the catalytic activity. So Fig. 6 showed the morphology of the nanofibers after the fifth catalytic reaction. It was clearly seen that the network of the nanofibers was generally kept intact. The TEM image revealed that the size of Ag/Pd nanoparticles on the surface of PAN nanofibers seemed to be a little smaller after the fifth catalytic reaction, which might be due to the corrosion during the reaction process.

4. Conclusions

In summary, we have demonstrated a simple but effective method for the fabrication of PAN/Ag/Pd nanofibers through

electrospinning technique and subsequent galvanic replacement reaction. The as-prepared PAN/Ag/Pd composite nanofibers exhibited excellent catalytic activity for the hydrolytic dehydrogenation of AB. Furthermore, the PAN/Ag/Pd composite nanofibers showed superior recycling stability which was still active after five times of recycling tests. Due to its special characteristic (membrane), it would be really convenient to circulating application especially in aqueous solution. And above all, the sense of our preliminary results provides a wide range of possibilities for the further development of green synthesis of air and water-stable catalysts in hydrogen generation which is of importance to our future society.

Acknowledgments

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